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Preparation and structure of double complex compounds $[La(HMPA)_4(NO_3)_2][Cr(NH_3)_2(NCS)_4]$

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Abstract

This paper presents the results of chemical analysis, IR- spectroscopic analysis, thermal gravitational analysis, X-ray phase analysis, and X-ray structural analysis, conducted to determine the composition, structure and properties of the double complex salts - tetra(isotiocyanato)diaminechromates(III) of complex lanthanon(III) of ceric group with hexamethylphosphorotriamide (HMPA) and nitrate-groups as ligands.

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Keywords: double complex salts (DCS), rare-earth elements (REEs), tetra(isotiocyanato)diaminechromates(III) ammonium, hexamethylphosphorotriamide (HMPA), X-ray structural analysis.

1. Introduction

Rare-earth elements (REEs), their chemical compounds and products based on rare-earth metals are of particular interest and strategic importance for the modern industrial world. These elements are used in computer, telecommunication and optical technologies, in radio electronics, nuclear technology and other high-tech fields[1-8].

The priority task is to expand and deepen the knowledge of chemical and physicochemical properties of the REEs, as well as the synthesis of new compounds based on them.

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Lack of information about peculiarities of formation and properties of double complex salts (DCS) contained in crystal structures tetra (isotiocyanato)diaminechromates (III) - anion and complex cation of REEs, with HMPA, stipulated interest in the current research.

Tetra (isotiocyanato)diaminechromates(III) ammonium (Reineke salt) is an anionic complex compound which can be considered as a source of matalloligands, particularly, of chromium (III) ions, ammonia molecules and rhodanide groups[9].

Hexamethylphosphorotriamide (HMPA) is widely used as a ligand of coordination compounds on the bases of various metals[10]. HMPA molecules can participate in coordination to a metal, protonated and hydrolyzed. It is possible to use compounds, containing an organic ligand, as precursors for making compositions of metal oxides, materials of the emissive layer[10]. The information of biological activity of lanthanoid compounds and the opportunities of their agricultural usage was obtained[10].

DCS can be obtained in solid state by means of direct synthesis from aqueous solutions[11].

2. Content

The fine-crystalline precipitates were obtained; the composition of precipitants according to chemical analyses corresponds to empirical formula $C_{28}H_{78}CrN_{20}LnO_{10}P_4S_4$. These precipitates were obtained during the studies of the aqueous solutions of lanthanoid (III) nitrates $Ln(NO_3)_3 \cdot 6H_2O$ line «C.P.», where Ln = La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} and Reineke salt $NH_4[Cr(NH_3)_2(NCS)_4] \cdot 0{,}5H_2O$, with molecular ratio 1:1, with later dropwise addition of organic ligand – HMPA, when pH is 6-7 and the solution's concentration is 0.05-0.5 mole/l.

The crystals are plate-shaped, with dimensions of 3-55 microns (Figure 1.). According to raster electron microscopy (SEM), X-ray structural analysis and X-ray fluorescence analysis it is possible to assume that the rare-earth elements are contained in the structure of compounds, do not form their own phase and are regularly distributed on the surface.

In order to determine the link between $Ln–O_{HMPA}$ the IR- spectroscopic analysis of the synthesized compounds is carried out. Group oscillations of double bonds (P=O) in free HMPA lie under 1350-1175 cm^{-1} [12]. These frequencies are recorded under 1302, 1262 cm^{-1} in spectra of the obtained compounds[13].

The decrease in the oscillation frequency group of P=O approximately by 60 cm^{-1} in comparison with the ligand spectrum indicates the electron density of the ligand molecule displacement to the central ion of the lanthanoid(III). Frequency of valence vibration (PNC) is shifted to higher values (992 cm^{-1}) in regard to oscillations in the free HMPA (982 cm^{-1}).

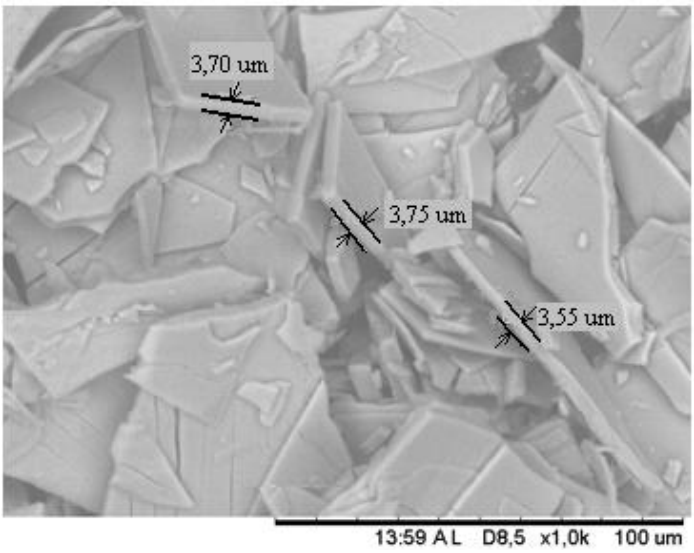

Fig. 1. SEM image of the surface of with tetra (isorhodanate)diaminechromate(III) lanthanon(III) with HMPA

X-ray structural analysis of the solid product of nitrate lanthanon(III) with tetra(isotiocyanato)diaminechromates(III) ammonium in hydro- hexamethylphosphorotriamide solution showed the existence of a new compound of ionic type $[La(HMPA)_4(NO_3)_2][Cr(NH_3)_2(NCS)_4]$, (Fig.2)[9]. It was found that the symmetry of the tested sample is described by the monoclinic space group $P2_1/n$, a=15.0360(3) Å, b=15.1214(3) Å, c=26.7529(7) Å, β=100.6610(10)°, V=5977.7(9) Å^3, Z=2, ρ =1.442 g/cm^3.

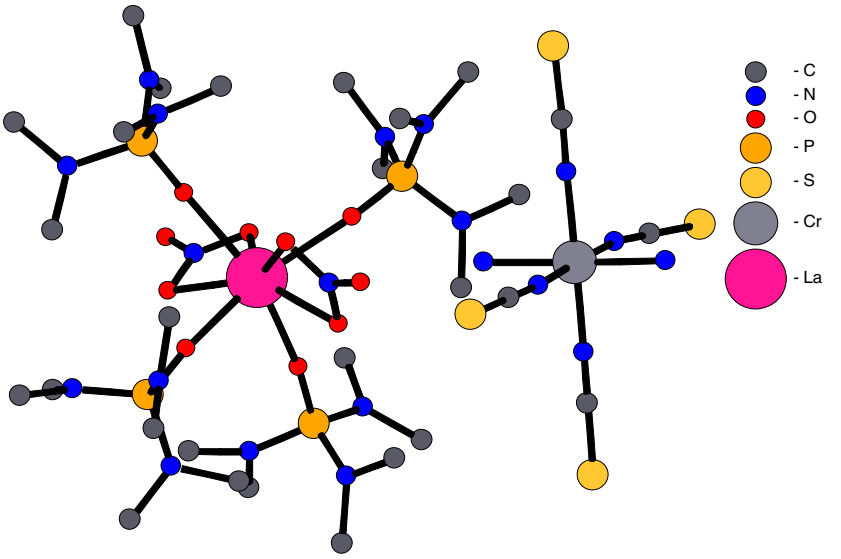

Fig. 2. Structure of compound $[La(HMPA)_4(NO_3)_2][Cr(NH_3)_2(NCS)_4]$, hydrogen atoms are not shown

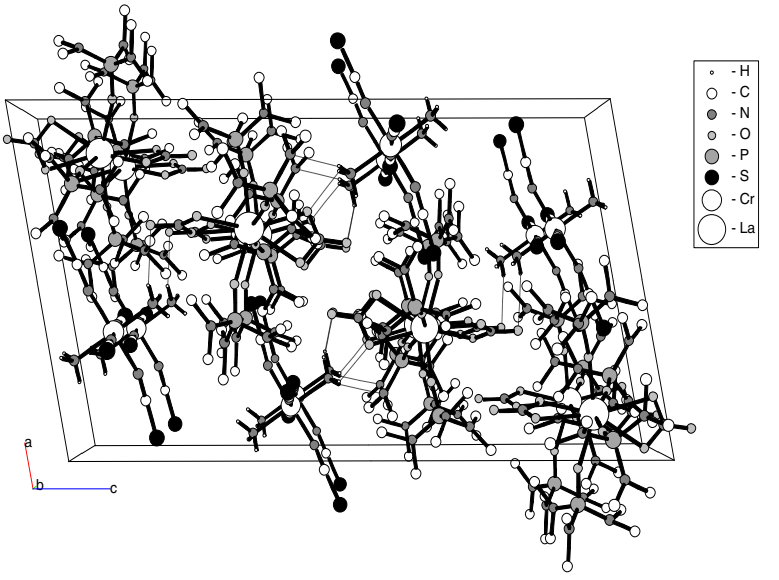

Fig. 3. Crystalline packing in $[La(HMPA)_4(NO_3)_2][Cr(NH_3)_2(NCS)_4]$

Ion La^{3+} coordinates 8 oxygen atoms – four atoms from the two NO_3-groups (La–O 2.599(3)-2.635(3) Å), and four – from four monodentate molecules HMPA (La–O 2.386 (3) -2.425 (3) Å). Bond lengths in the molecule HMPA are P=O 1.498(3)-1.503(3) Å; P–N 1.620(4)-1.653(4) [10,14].

In the crystal packing of compound $[La(HMPA)_4(NO_3)_2][Cr(NH_3)_2(NCS)_4]$ the system of hydrogen bonds occurs (Fig. 3). Anion $[Cr(NH_3)_2(NCS)_4]^-$ hydrogen-bonds: NH_3-groups with two molecules HMPA, one oxygen atom of one of the NO_3-groups and two oxygen atoms of the second NO_3-group.

The compounds thermolysis process involves several stages (Fig. 4). Exothermic peak in the temperature range 95-130°C corresponds to the decomposition of the complex with elimination and burning of ammonia molecules and the beginning of HMPA molecules removal. On IR-spectra of the decomposition products under 200°C, there is a decrease in intensity of the absorption bands of valence vibration of NH-groups (3222, 3151 cm^{-1}) and group P-O (1302, 1262 cm^{-1}).

The main mass loss occurs in the range of 200-500°C. On the curve of differential scanning calorimetry DSC the range is represented by two exo-effects with extreme values due to samples decomposition and products of decomposition burning.

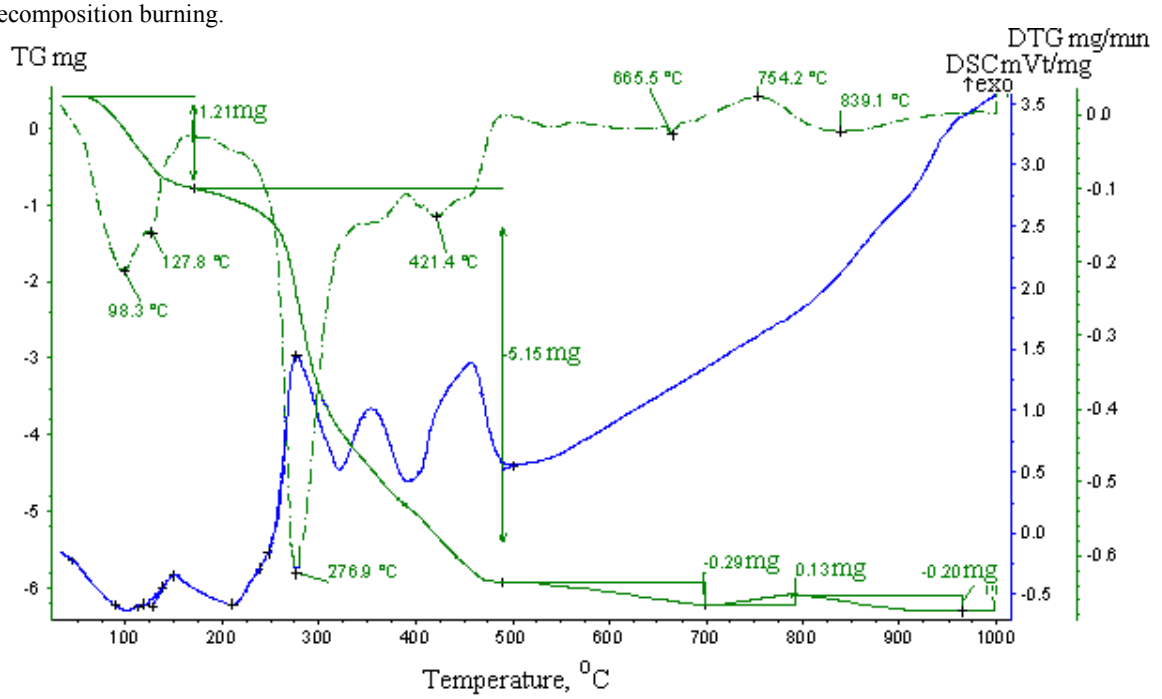

Fig. 4. Thermogramm of compound banding $[La(HMPA)_4(NO_3)_2][Cr(NH_3)_2(NCS)_4]$ on air

3. Conclusions

By varying such parameters as media acidity, concentration ranges and temperature compound compositions were obtained from aqueous solutions: $[Ln(HMPA)_4(NO_3)_2][Cr(NH_3)_2(NCS)_4]$, where Ln = La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, HMPA – hexamethylphosphortriamide $((CH_3)_2N)_3PO$. Isostructurality of obtained substances was proved due to the similarity of diffraction patterns, infrared spectra and picnometer density. X-ray structure analysis method for the direct determination of the structure $[La(HMPA)_4(NO_3)_2][Cr(NH_3)_2(NCS)_4]$ was successfully applied. X-ray diffraction characteristics and properties of the compounds may be used to conduct chemical analysis of crystals and to describe physicochemical properties, as well as their dependence on the various factors. It was determined that the thermal decomposition of DCS proceeds at relatively low temperatures without reversible color changes in the investigated temperature range.

The obtained results contribute to the fundamental knowledge of REE and also bring us closer to the controlled synthesis of new applicable materials.

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